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Method and apparatus for determining the  
presence of oxygen

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FIG. 1

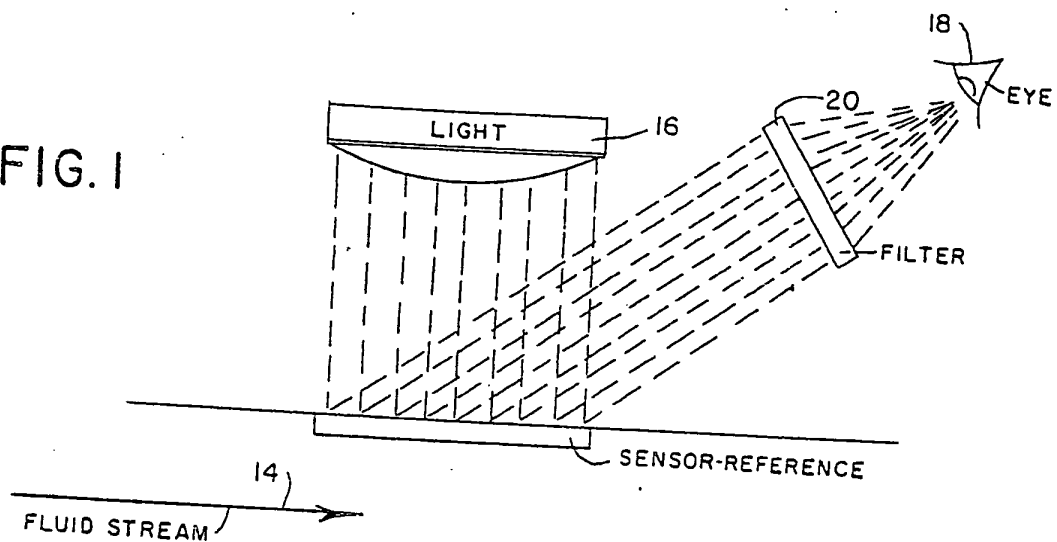


FIG. 2

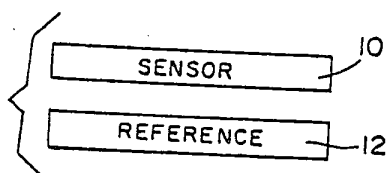


FIG. 3

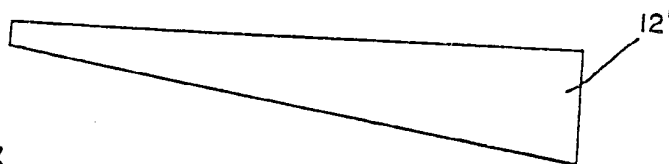


FIG. 4



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METHOD AND APPARATUS FOR DETERMINING THE PRESENCE OF OXYGEN

This invention relates generally to a method and apparatus for determining the presence and concentration of oxygen in a gaseous or liquid environment and is based on the principle of luminescence quenching.

5       The two most common methods currently used for determining oxygen concentrations are the Winkler titration method and the oxygen electrode method. The Winkler method is slow, intrusive, destroys the sample and does not lend itself to automation. The oxygen electrode method consumes oxygen, is sensitive to  
10   interferants such as Halothane anesthetic, is intrusive, and is not readily applicable to the gas phase or vacuum systems. Hence, neither of these methods is particularly desirable.

      It is known that many platinum group metal complexes luminesce intensely in the red region (600-650 nm) when excited  
15   with visible light or UV light (< 550 nm). Both the intensity and the lifetime of the luminescence is decreased when the complex is exposed to deactivators (quenchers). Oxygen, iron (III), copper (II), and mercury (II) are among the common quenchers. When a single quencher is present in  
20   an environment, the degree of intensity or lifetime quenching is directly related to the quencher concentration and can be used as an analytical method for determining that concentration. However, the inability of the method to discriminate among different quenchers in an environment has heretofore  
25   prevented the method from being universally applicable.

      The discrimination problem is particularly acute when dealing with a liquid environment. If the luminescent complexes are dissolved directly in the solution, a variety

of dissolved organic and inorganic, contaminants and interferents would contribute to the quenching and would produce an erroneous indication of the oxygen concentration.

Because the luminescence quenching method presents the possibility of making oxygen determinations without the limitations inherent in the Winkler titration method and the oxygen electrode method, it is desirable to improve upon known methods and apparatus in the luminescence quenching art in order to make that method universally applicable.

Examples of pertinent patents are U.S. Patent Nos. 998,091; 1,456,964; 2,351,644; 2,929,687; 3,112,999; 3,697,226; 3,725,658; 3,764,269; 3,768,976; 3,881,869; 3,897,214; 3,976,451; 4,054,490; 4,073,623; 4,089,797; 4,181,501; 4,231,754; 4,260,392; 4,272,249; 4,272,484 and 4,272,485.

U.S. Patent 3,725,658 shows a method and apparatus for detecting oxygen in a gas stream. The apparatus employs a sensor film comprising a fluorescent material dissolved in a carrier or solvent and supported on a substrate. Oxygen contained in the gas stream is dissolved into the film and quenches the fluorescent emission, the extent of quenching being proportional to the oxygen content of the gas stream.

U.S. Patent 3,764,269 shows the use of a gas permeable membrane which permits diffusion of a particular gas while providing protection against the adverse effects of the environment. An electrochemical device detects the concentration of gas which passes through the porous layer and activates the electrode.

U.S. Patent 3,881,869 discloses the chemiluminescent detection of ozone concentration in a gas sample. The gas sample contacts an organic polymer having a backbone chain consisting of carbon atoms to produce a chemiluminescent reaction. The concentration of ozone is proportional to the intensity of light emitted by the reaction.

U.S. Patent 4,089,797 discloses chemiluminescent warning capsules having an air-reactive chemiluminescent formulation encapsulated with a catalyst. Crushing the capsule mixes the air-reactive formulation and the catalyst in the

external environment to produce chemiluminescence if air is present.

5 U.S. Patent 4,272,484 uses fluorescence methods to measure oxygen content after first separating blood protein fractions and other components by use of a gas permeable membrane. U.S. Patent 4,272,485 is a related disclosure which includes a carrier which transports particles through the membrane.

10 U.S. Patent 3,112,999 discloses a gas, particularly carbon monoxide, which permeates a porous layer to make an indication.

U.S. Patent 2,929,687 discloses a dissolved oxygen test.

U.S. Patent 3,768,976 shows a polymeric film through which oxygen migrates to cause an indication.

15 U.S. Patent 3,976,451 describes selectively permeable membranes for passing oxygen.

U.S. Patent 4,260,392 shows a selectively permeable plastic tape.

20 U.S. Patent 3,897,214 discloses reagents impregnated in plastic fibres.

U.S. Patent 3,697,266 discloses a system using a graded scale for visual comparison. The comparison scale is not placed in a solution. It is merely a screen.

25 U.S. Patent 998,091 discloses a colour comparing scheme in which thickness is varied in a graded standard.

U.S. Patents 4,181,501 and 4,054,490 disclose wedge shaped concentration sensors.

U.S. Patent 2,351,644 discloses a stepped sensor.

30 U.S. Patent 4,073,623 discloses a non-immersed sensor and standard used for visual comparisons.

U.S. Patent 1,456,964 discloses light intensity comparison. The remaining patents are of lesser interest.

The following publications are also of interest:

35 Energy Transfer in Chemiluminescence, Roswell, Paul and White, Journal of the American Chemical Society, 92:16, August 12, 1970, pp.4855-60; Oxygen Quenching of Charge-Transfer Excited States of Ruthenium (II) Complexes. Evidence for Singlet Oxygen Production, Demas, Diemente and Harris, Journal

- of the American Chemical Society, 95:20, October 3, 1973, pp.6864-65; Energy Transfer from Luminescent Transition Metal Complexes to Oxygen, Demas, Harris and McBride, Journal of the American Chemical Society, 99:11, May 25, 1977, pp. 3547-3551; Britton, Hydrogen Ions. Their Determination and Importance in Pure and Industrial Chemistry, D Van Nostrand Company, Inc. (1943) pp.338-43; and Fiberoptics Simplify Remote Analyses, C&EN, September 27, 1982, pp.28-30. Porphyrins XVIII. Luminescence of (Co), (Ni), Pd, Pt Complexes, Eastwood and Gouterman, Journal of Molecular Spectroscopy, 35:3, September 1970, pp.359-375; Porphyrins XIX. Triplet and Quartet Luminescence in Cu and VO complexes, Gouterman, Mothies Smith and Caughey, Journal of Chemical Physics, 52:7, April 1, 1970, pp 3795-3802; Electron-Transfer Quenching of the Luminescent Excited State of Octachlorodirhenate(III), Nocera and Gray, Journal of the American Chemical Society 103, 1971, pp.7349-7350; Spectroscopic Properties and Redox Chemistry of the Phosphorescent State of  $Pt_2(P_2O_5)_4Hg^{4-}$ ; Che, Butler, and Gray, Journal of the American Chemical Society 103, 1981, pp.7796-7797; Electronic Spectroscopy of Diphosphine- and Diarsine-Bridged Rhodium (I) Dimers, Fordyce and Crosby, Journal of the American Chemical Society 104, 1982, pp.985-988.
- The Demas, et al articles disclose oxygen quenching of  $\Delta$ -diimine complexes of Ru(II), Os(II), and Ir(III). 2, 2'-Bipyridine, 1, 10-phenanthroline and substituted derivatives are used as ligands to form the metal-ligand complexes. A kinetic mechanism for the complex oxygen interaction is proposed.
- The Roswell article discusses intermolecular energy transfer in chemiluminescence.
- The Britton publication discloses a wedge method for the determination of indicator constants of two-colour indicators.
- The C&EN article deals with PTFE control membranes in the context of laser optrodes and optical fibres.
- The Eastwood article describes the room temperature luminescence and oxygen quenching of Pd and Pt porphyrin complexes in fluid solutions.

The Gouterman et al, article describes low temperature luminescence of Cu and VO porphyrins. Extrapolation of their data to room temperature indicates oxygen quenchable lifetimes.

5 The Nocera paper reports quenching of dinuclear Re species. Mononuclear and dinuclear Re complexes also have quenchable excited states.

The Che paper reports long excited state lifetimes and solution oxygen quenching of a dimeric Pt complex in solution and long-lived quenchable excited states of Rh dimers.

10 The Fordyce reference reports long-lived low temperature emissions of Rh(I) with bridging ligands. Rh(I) and Ir(I) data are referenced. Extrapolation of their data to room temperature suggests oxygen quenchable lifetimes.

15 It is an object of the present invention to provide a method and apparatus which substantially overcomes the problems which exist in the prior art.

According to a first aspect of the present invention, this provides a method for determining the presence of oxygen in an environment comprising providing luminescent inorganic material  
20 which luminesces when excited by visible or ultra-violet light and whose intensity and lifetime of luminescence is quenchable by oxygen, incorporating said material in a carrier material which is relatively permeable to oxygen and relatively impermeable to interfering quenchers, thereby forming a sensor,  
25 exposing the sensor to an environment to be sampled, allowing oxygen in the environment to permeate the carrier material and quench the luminescent material, measuring the quenching-related decrease in intensity or lifetime of luminescence by comparing it with a reference luminescent material, and  
30 determining the presence of oxygen based on the measured quenching.

The oxygen concentrations can be in liquid solutions or in the gas phase. The method is based on the shortening of the lifetime or decrease in the emission intensity, i.e.  
35 quenching, of particular metal complexes, preferably ruthenium (II) complexes with  $\alpha$ -diimine ligands in the presence of oxygen. The oxygen concentrations can be directly related to the degree of quenching. To prevent the complexes from

responding to contaminants and interferents, the complex is protected by being immobilized in a gas permeable, solvent impermeable polymer, such as silicon rubber.

5 The oxygen determination method of the invention may be modified to provide a method of oxygen determination which is based on a quantitative quencher related decrease in the luminescence intensity of a luminescent material.

10 According to a second aspect of the present invention sensor apparatus for determining the presence of oxygen in an environment includes a first and a second element each of which luminesces when excited by visible or ultra-violet light, the luminescence shown by said first element having an intensity and lifetime quenchable by oxygen, the first  
15 element comprising luminescent inorganic material incorporated in a carrier material which is relatively permeable to oxygen and relatively impermeable to interfering quenchers and the second luminescent element comprising luminescent  
20 inorganic material incorporated in a carrier material which is relatively impermeable to both oxygen and interfering quenchers in order to act as a reference to an adjacent luminescent material. This provides an oxygen concentration sensor and a graded calibration reference which can be  
25 visually compared to determine oxygen concentration. The sensor is a fluorophor immobilized in oxygen-permeable polymer. The graded calibration reference is either tapered with thicker (brighter) portions corresponding to lower oxygen concentrations on the sensor or with higher (brighter) concentrations of a fluorophor at one end of  
30 the standard. The sensor and reference are exposed to the environment being sampled and are excited by a light source. Intensity of the light emitted by the sensor is decreased by the oxygen. The eye is used to determine the part of the reference that has the same brightness as the sensor.

35 The oxygen sensor may have a platinum group metal complex with  $\chi$ -diimine ligands immobilized in an oxygen permeable polymer which tends to prevent interfering quenchers from interacting with the complexes.



Both the method and apparatus of the invention provide an inexpensive way of visually determining the extent of quenching.

The method and apparatus of the invention will now be described, by way of example only, with reference to the accompanying drawings. In the drawings:

Figure 1 is a schematic diagram, in side view, of a visual oxygen monitoring system embodying features of the present invention,

Figure 2 is a top plan view of sensor and reference devices shown in Figure 1,

Figure 3 is a detailed schematic diagram of a reference device used with the system shown in Figures 1 and 2, and

Figure 4 is a detailed schematic diagram of an alternative reference device used with the system shown in Figures 1 and 2.

The method of the invention is based on the principle of shortening of the lifetime or decrease in the emission intensity (quenching) of certain luminescent materials in the presence of oxygen. The oxygen concentrations can be directly related to the degree of quenching in a manner well known in the art.

The luminescent materials are luminescent inorganic materials which luminesce when excited with visible or ultraviolet light and whose luminescence is quenchable by oxygen and other quenchers.

The preferred luminescent materials are principally platinum group metal complexes, specifically, ruthenium, osmium, iridium, rhodium, palladium, platinum, rhenium and chromium complexes with  $\beta$ -diimine ligands. In most instances, the tris complexes are used, but it is recognized that mixed ligand complexes can also be used to provide a degree of design flexibility not otherwise available. Suitable ligand metal complexes include complexes of ruthenium(II), osmium(II), iridium(III), rhodium(III), and chromium(III) ions with 2,2'-bipyridine, 1,10-phenanthroline, 4,7-diphenyl-(1,10-phenanthroline), 4,7-dimethyl-1,10-phenanthroline, 4,7-disulfonated-diphenyl-1,10-phenanthroline, 5-bromo-1,

10-phenanthroline, 5-chloro-1, 10 phenanthroline, 2,2'-bi-2-thiazoline, 2,2'bithiazole, and other  $\Delta$ -diimine ligands.

Other suitable systems could include porphyrin or phthalocyanine complexes of  $\text{VO}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pt}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pd}^{2+}$  OR  
5 dimeric Rh, Pt, or Ir complexes and also dicyano complexes. Suitable ligands would be etioporphyrin, octaethylporphin, porphin and phtalocyanine.

To prevent the complexes from responding to contaminants and interferences, the complex is protected by being immobilized  
10 in a gas permeable, solvent impermeable polymer. Preferred polymers include glass polymer such as Plexiglas<sup>®</sup> (RTM), polyvinyl chloride (PVC), polystyrene, polycarbonate, latex, fluorinated polymers such as that known under the registered Trade Mark Teflon, and silicon rubbers, such as GE RTV  
15 SILASTIC 118 (RTM), which is very temperature resistant. A sensor using SILASTIC 118 (RTM) exhibits a substantial change in lifetime or intensity of luminescence on going from an oxygen saturated environment to a deoxygenated environment. The precision and accuracy of oxygen determinations is about  
20 2 per cent and the same responses are obtained for both lifetime and intensity quenching measurements. It responds rapidly to changes in both gas phase and solution dissolved oxygen concentrations. The Plexiglass (RTM) and PVC systems have lower oxygen sensitivities and are, thus, suitable for  
25 determinations at high (above atmospheric) oxygen pressures. Commercially available silicon rubber has a high permeability of oxygen and excludes highly polar compounds and hydrated ions which is why its use in the present invention is desirable.

30 The preferred oxygen sensor used tris(4,7-diphenyl-1,10-phenanthroline ruthenium(II) dissolved in the SILASTIC 188 (RTM) material.

The luminescent complexes can be uniformly diffused into the polymer from dichloromethane and/or alcohol solutions.  
35 Alternatively, the complexes can be mixed with the polymer before final polymerization.

The metal complexes can be mechanically or chemically incorporated into the polymer matrix. In one embodiment, the complex molecules are chemically attached to the backbone of the matrix. Either a covalent or an ionic attachment of the complex to the polymer can be used. For example, cation exchange bound RU(II) complexes exhibit high sensitivity to gas phase oxygen quenching.

The completed sensor is an integral device having the luminescent material incorporated directly into the self-supporting polymer barrier system. It can be in the form of a strip, a block, a sheet, a microsphere, a film or a laminate and it can be either solid or hollow. If desired, the sensor can be a thin sensing layer diffused onto a thick plate. An overcoat of a less reactive polymer can be used to further reduce interactions with the solvent or quenchers.

In one embodiment, a thin film sensor is formed by leaching sodium from glass to form a porous matrix, dipping the glass into a solution of luminescent material and then covering the surface of the glass with a layer impermeable to water. Suitable agents are silicon water proofing which reacts with the surface or polymer overcoats.

To reduce expenses, it is desirable that the sensor be in the form of reusable polymer coated cuvettes which are highly durable.

In use, the sensor is exposed to the liquid or gaseous environment being sampled. Because the polymer material has a relatively high permeability to oxygen, the oxygen will permeate through the material and interact with the luminescent material to act as a quencher. However, the polymer will exclude most common ionic and organic interferents and contaminants.

The quenching-related decrease in the intensity or lifetime of luminescence is measured and that measurement is used to determine the concentration of oxygen in the environment. By measuring the luminescence lifetime or intensity using a back scattering technique, interferences caused by strong scattering or absorbing solution are eliminated.

In an alternative embodiment, the sensor is excited by a modulated light source and a phase shift measurement is made of the luminescence to yield the lifetimes.

5 The present invention provides a particularly desirable means for oxygen determination because it is non-invasive and does not consume oxygen. It is usable over an extremely wide range of oxygen concentrations or partial pressures and readily lends itself to miniaturized and automated analyses.

10 Test results have demonstrated that the present invention is sensitive, selective and readily implemented. With the preferred combination of metal complex and polymer matrix, a material has been prepared that shows a 3000% increase in luminescence lifetime on going from an oxygen saturated aqueous environment to a nitrogen saturated environment. Response  
15 time is subsecond to minutes depending on film thickness. The same complex-polymer sensor responds equally well to gas phase oxygen concentrations. Films of 0.001" thickness have been shown to respond in <1/6 sec. and follow faithfully the oxygen concentration in the breath of a human.

20 The ability of the polymer to protect the complex from interferents was shown by introducing a film into a concentrated solution of iron(III). Normally iron(III) is an excellent quencher of unprotected complexes. Yet, even at the high iron(III) concentrations used, there was no  
25 detectable quenching. Strong acid strong base, complexing agents (EDTA), and detergents (NaLS) were likewise without effect. The sensor is also immune to any deactivation by common anaesthetic gases such as Halothane and nitrous oxide at concentrations well above those used medically.

30 Applications for the present invention include:  
(1) measuring dissolved oxygen in aqueous samples and in organic solvents; (2) determining the oxygen for biochemical oxygen demand (BOD) measurements; (3) measuring levels of oxygen in blood both in vitro and in vivo using a fibre-optic  
35 probe; (4) measuring oxygen levels in air samples (e.g., mines, industrial hazard areas, oxygen tents, high pressure oxygen burn treatment and decompression chambers, industrial

reactors space capsules etc); (5) measuring low oxygen levels in vacuum systems (i.e., a low-cost vacuum gauge); and (6) monitoring low oxygen levels in various chemical reaction vessels, e.g. glove boxes and other systems purged with inert gas.

An application in Category 1 would include pollution monitoring of waste water.

The application in Category 2 is especially interesting in view of the above described test using iron(III). Iron (III) is added as a nutrient in BOD determinations. However, the test showed that iron(III) concentrations hundreds of times larger than would be encountered in BOD analyses have no detectable quenching effect. BOD determinations using quantitative intensity monitoring have been implemented.

The Category 3 applications could involve, for example, the placing of a sensor at the end of a fibre optic catheter for use in following oxygen concentrations in blood vessels and tissues as the heart is beating. Such a system has great safety as there is no electrical connection to the patient.

Advantages of the present invention are that it is a non-destructive and relatively non-intrusive method and that a common system can be used to measure oxygen in polluted, murky water, air samples, vacuum systems and other diverse types of systems. The invention is operable over a temperature range of about -300°F to about 400°F.

In addition, the system lends itself readily to measurements on very small sample size (<50μL), instrumental miniaturization, and automation. By encapsulating the complex probe in microscopic beads, oxygen concentrations can be measured under a microscope in growing cellular samples.

Quantitative intensity and lifetime methods for measuring oxygen concentrations are accurate and precise. There are many times, however, when a semiquantitative or qualitative method of even lower cost is desirable.

To avoid the cost of a more elaborate instrument the present invention further provides a low cost visual

detection system with an internal reference for semiquantitative or qualitative oxygen monitoring.

In the present invention, the human eye is used as the detector. The scheme is similar in application to pH paper except that one monitors oxygen concentrations by comparing the emission intensity of the sensor in the gas or liquid environment to a series of reference emitters in that environment. Although suitable for semi-quantitation of oxygen concentrations, the system is also usable as a go - no go system where instantaneous visual discrimination between pure oxygen, air, or an oxygen-free system is required.

A schematic diagram of this system is shown in Figures 1 to 4 to which reference is now made.

A luminescent oxygen sensor 10 and a reference emitter 12 are placed side-by-side in the sample fluid or gas environment 14. The sensor 10 includes a fluorophor immobilized in an oxygen-permeable support, in this example, a polymer. The sensor 10 luminesces when the fluorophor is excited by a light source 16. The intensity of the emitted light is decreased by oxygen in the environment 14 which serves as a quencher.

The human eye can easily judge the differences in intensity of the emitted light when the sensor film is exposed to pure  $N_2$ , air and  $O_2$  environments.

The estimation of the oxygen concentration beyond air,  $O_2$  or  $N_2$  is improved by using a reference emitter 12 which is a concentration or optical density graded calibration standard. In the standard, the same fluorophor as used in the sensor 10 would be immobilized in a rigid polymer, for example that known under the Trade Name Plexiglass, which shows limited permeability to  $O_2$ . The fluorophor is distributed in the polymer in areas having different luminescence levels.

The reference emitter 12 next to the sensor 10 provides reference concentration information by emitting reference luminescence levels. The differences in luminescence between the sensor 10 and the reference 12 are visually determined by the human eye 18. An optional blocking filter 20 can be positioned between the eye 18 and the sensor 10 and reference

12 to improve viewing contrast by removing scattered excitation light. In addition, a filter (not shown) over the light source may be used to improve viewing by limiting excitation wavelengths.

5        In one embodiment, the standard 12' has a tapered wedge shape as shown in Figure 3. The luminescence intensity at each point is determined by the thickness of the standard 12'. The thicker (brighter) portions correspond to lower oxygen concentrations on the sensor 10. A non-uniform slope on the  
10 wedge improves the linearity of calibration.

      In an alternative embodiment, the standard 12'' is a concentration graded reference with the concentration of fluorophor contained therein increasing from one end to the other. The higher (brighter) concentrations correspond to  
15 lower oxygen concentrations on the sensor. In the graded standard 12'' shown in Figure 4, the relative concentration of the fluorophor is indicated by the dot density. The sensor 12'' is of uniform thickness.

      The graded concentration standard 12'' can be formed by  
20 withdrawing a polymer film from a solution containing the fluorophor material. The areas of the film which remain longer in the solution contain greater concentrations of the fluorophor. In a further embodiment (not shown) the standard can be staircase shaped and the steps may be non-uniform.

25        In the preferred embodiment, the sensor 10 and the reference 12 are formed of identical luminescent materials. This ensures that the emission colours are the same and that the observer will only be comparing intensities.

      Fluorophors suitable for use in the present invention  
30 include, but are not limited to, the metal complexes discussed above. The preferred material is tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) immobilized in a silicon rubber polymer matrix.

      The system shown in the figures is used by allowing the  
35 oxygen in the environment 14 to impinge upon the sensor 10 and reference 12. The support matrix in the sensor 10 is permeable to oxygen, and thus allows the oxygen to quench the

luminescent material. The matrix in the reference 12 restricts oxygen access to the fluorophor material therein. The luminescence of the quenched sensor 10 is then compared to the luminescence of the reference 12. The area of the reference 12 having the same luminescence as the sensor 10 is then visually selected. Knowledge of the amount of luminescent material present in the selected area is used to determine the amount of oxygen present in the environment 14. With proper calibration, a visual match of emission intensity can allow oxygen estimations to within a few per cent.

For sensor 10, films of 0.001" thickness, the response time is subsecond. Thicker sensor films respond more slowly and provide indications of average oxygen concentrations.

The referencing systems described above are inexpensive and provide stable, long-lasting, rapid monitors for gaseous or liquid oxygen levels. They can be incorporated into operating room gas lines, breathing masks, and other hospital devices where the shut-off or improper connection of oxygen could be fatal. They can also be used in mines and industrial areas where oxygen levels vary. Applications as far-reaching as space capsules and as ordinary as welding machines (He-arc purges) are also contemplated.



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CLAIMS:

1. A method for determining the presence of oxygen in an environment comprising providing luminescent inorganic material which luminesces when excited by visible or ultra-violet light and whose intensity and lifetime of luminescence is quenchable by oxygen, incorporating said material in a carrier material which is relatively permeable to oxygen and relatively impermeable to interfering quenchers, thereby forming a sensor, exposing the sensor to an environment to be sampled, allowing oxygen in the environment to permeate the carrier material and quench the luminescent material, measuring the quenching-related decrease in intensity or life-time of luminescence by comparing it with a reference luminescent material, and determining the presence of oxygen based on the measured quenching.
2. A method as claimed in Claim 1 wherein the environment is a gas.
3. A method as claimed in Claim 1 wherein the environment is a liquid.
4. A method as claimed in any preceeding claim wherein the concentration of oxygen in the environment is determined.
5. Sensor apparatus for determining the presence of oxygen in an environment including a first and a second element each of which luminesces when excited by visible or ultra-violet light, the luminescence shown by said first element having an intensity and lifetime quenchable by oxygen, and the first element comprising luminescent inorganic material incorporated in a carrier material which is relatively permeable to oxygen and relatively impermeable to interfering quenchers, and the second element comprising luminescent inorganic material incorporated in a carrier material which is relatively impermeable to both oxygen and interfering quenchers in order to act as a reference.
6. Apparatus according to Claim 5 wherein the luminescent material is a phosphorescent material.
7. Apparatus according to Claim 5 wherein the luminescent material is a platinum group metal complex.
8. Apparatus according to Claim 5 wherein the luminescent material is selected from vanadium, copper, ruthenium, rhenium, osmium, iridium, rhodium, platinum, palladium, zinc and chromium complexes with  $\chi$ -diimine ligands, porphyrins, phthalocyanine and other ligands.

9. Apparatus according to Claim 8 wherein the complexes are selected from mixed ligand complexes, dicyano complexes and tris complexes.
10. Apparatus according to Claim 8 wherein the luminescent material is selected from complexes of ruthenium(II), osmium(II), iridium(III), rhodium, rhenium, and chromium(III) with 2,2'-bipyridine, 1, 10-phenanthroline, 4,7-diphenyl(1,10-phenanthroline), 4,7-dimethyl-1, 10-phenanthroline, 4,7-disulfonated-diphenyl-1, 10-phenanthroline, 2,2'-bi-2-thiazoline, 2,2'-bithiazole, 5-bromo-1,10-phenanthroline, and 5-chloro-1,10-phenanthroline and complexes of  $\text{VO}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pt}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Pd}^{2+}$  with porphin, etioporphorin, phthalocyanine and octaethylporphyrin.
11. Apparatus according to Claim 8 wherein the luminescent material comprises tris(4,7-diphenyl-1,10-phenanthroline)-ruthenium(II), tris(disulfonated-(4,7-diphenyl-1),10-phenanthroline)ruthenium(II), and (disulfonated-4,7-diphenyl-1, 10-phenanthroline)bis(1,10-phenanthroline)-ruthenium(II).
12. Apparatus according to any one of Claims 5 to 11 wherein the carrier material comprises a polymer in the form of sheets, films, blocks, laminates, microspheres and strips which are solid or hollow.
13. Apparatus according to Claim 12 wherein the polymer is selected from the group consisting of glass polymer, polyvinyl chloride, silicon rubber, latex rubber, polycarbonate, fluoridated polymers, polystyrene, polyvinylidene fluoride, polytetrafluoroethylene propylene and cation and anion exchange resins.
14. Apparatus according to Claim 12 or 13 wherein the luminescent material is incorporated into the polymer by a process selected from the group consisting of diffusing the luminescent material into the polymer from suitable organic solution, mixing the luminescent material with the polymer before final polymerization, and ionically or covalently binding the luminescent material to the polymer.

15. Apparatus according to any of Claims 12 to 14 wherein the polymer is protected further from the solvent by over-coating it with an oxygen permeable solvent resistant polymer such as a fluorinated polymer.

5 16. Apparatus according to any one of Claims 5 to 11 wherein the carrier material comprises a porous adsorbant polymer such as silica gel or controlled porosity glass.

10 17. Apparatus according to Claim 16 wherein the luminescent material is incorporated into the adsorbant by diffusion from a penetrating solvent and held by adsorption, ionic binding or covalent chemical attachment to the adsorbant.

15 18. Apparatus for determining the amount of oxygen in an environment comprising sensor apparatus as claimed in any one of Claims 5 to 17, the second element having said luminescent material distributed therein in areas having differing amounts of said material, said first and second elements being arranged in a proximate relationship, said first and second elements being arranged to be exposed to an environment to be sampled.

20 19. Apparatus according to Claim 18 wherein the reference comprises the carrier material having luminescent material distributed therealong in areas having differing amounts of said luminescent material, said luminescent material being the same as that in the first element.

25 20. Apparatus according to Claim 19 wherein said luminescent material in said reference is distributed in areas of differing thickness.

30 21. Apparatus according to Claim 19 or 20 wherein the reference has a wedge or staircase shape, the amount or luminescent material present in any portion of said wedge or staircase being related to the thickness of said portion.

22. Apparatus according to Claim 21 wherein the wedge or staircase has a non-uniform slope or step size.

35 23. Apparatus according to any of Claims 19 to 22 wherein the luminescent material in said reference is distributed to form areas having differing concentrations of said luminescent material.

24. Apparatus according to any of Claims 18 to 23 wherein the luminescent material comprises fluorophor material.

25. Apparatus according to any one of Claims 18 to 24 wherein the reference is formed by withdrawing the carrier material from a solution of luminescent material, the concentration of luminescent material in a given area of the carrier material being related to the length of time the area remains in said solution.

26. Apparatus as claimed in any of Claims 5 to 25 in which the carrier material contains a mixture of luminescent materials quenchable by oxygen, said materials of the mixture having differing sensitivities to oxygen quenching and having differing colours of emission.

27. A method of determining the amount of oxygen in an environment comprising employing sensor apparatus as claimed in any of Claims 5 to 17, the reference of the apparatus having said luminescent material distributed therein in areas having differing amounts of said material, said first and said second elements being arranged in a proximate relationship, comprising <sup>exposing</sup> said first and second elements to <sup>the</sup> ~~an~~ environment ~~to be sampled~~, and comparing the luminescence of the first element with the luminescence of an area of the reference to determine the amount of oxygen in the environment based on the amount of luminescent material present in said area of the reference.

28. A method of determining the presence of oxygen in an environment substantially as hereinbefore described, and with reference to Figures 1, 2 and 3 or Figures 1, 2 and 4 of the accompanying drawings.

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